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A structure–activity relationship for pincer palladium(II) complexes — influence of ring-size of metallacycles on the activity in allylic alkylation

Zhaohui Wang [a], Michael R. Eberhard [a,*], Craig M. Jensen [a], Shiro Matsukawa [b], Yohsuke Yamamoto [b,1]

[a] Department of Chemistry, University of Hawaii, 2545 The Mall, Honolulu, HI 96822-2275, USA
[b] Department of Chemistry, Graduate School of Science, Hiroshima University 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan

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Abstract

A series of new palladium(II) complexes derived from the well-known pincer complex [PdCl{(C_6H_3)(OP^iPr_2)$_2$-2,6}] were synthesised: [PdX{(C_6H_3)(OP^iPr_2)$_2$-2,6}] (X = Br^-, I^-, OAc^-, OTf^-). A novel PCP′ pincer ligand 1-($^iPr_2PO$)-3-($^iPr_2POCH_2$)(C_6H_4) was prepared and complexed to palladium(II) to give [PdX{(C_6H_3)(OP^iPr_2)-2-($CH_2OP^iPr_2$)-6}] (X = Cl^-, I^-, OAc^-, OTf^-, BF_4^-). The X-ray structure of [PdCl{(C_6H_3)(OP^iPr_2)-2-($CH_2OP^iPr_2$)-6}] was solved and is discussed. These complexes were applied to the catalytic reaction of cinnamyl acetate with sodium dimethyl malonate in order to evaluate the influence of the ligand structure and co-ordinating or non-co-ordinating anions on the regioselectivity. A detailed analysis shows that palladium(II) complexes of the unsymmetrical PCP′ bis(phosphinito) ligand are much more active when compared to related complexes of the symmetrical PCP bis(phosphinito) ligand. The origin of this difference in activity is discussed.

Keywords: Phosphorus; Pincer; Palladium; PMP angle; Allylic alkylation

1. Introduction

PCP pincer ligands, monoanionic terdentate ligands with the general formula [(C_6H_3)(APR_2)$_2$]$^-$ (A = CH_2, O), have received great attention since the first example was reported by Moulton and Shaw [1]. Their chemistry has been reviewed recently [2]. PCP pincer complexes were found to be active catalysts for a wide range of reactions including dehydrogenation [3], transfer dehydrogenation [4], Heck reaction [5], Suzuki-coupling [6], Negishi-type coupling [7] and enantioselective sharpless epoxidations [8]. Pincer ligands bond most commonly in the meridional η^3-PCP co-ordination mode to metals, which is the reason for their great air-, temperature- and moisture-stability. Most pincer ligands are based on one-atom linkages between the donor atom P and the aryl-carbon. Thus, upon metal complexation the ligand forms two five-membered metallacycles. Venanzi and co-workers recently reported the synthesis of [MBr{(C_6H_3)((CH_2)$_2PPh_2$)$_2$-2,6}] (M = Pd, Pt), which is the only example for a PCP pincer ligand forming two six-membered metallacycles [9].

We previously reported on the synthesis and applications of [PdCl{(C_6H_3)(OP^iPr_2)$_2$-2,6}] (**1**) [5c,5d,7]. Ligand exchange furnished the following new complexes: [PdX{(C_6H_3)(OP^iPr_2)$_2$-2,6}] (X = Br^- **2**, I^- **3**, OTf^- **4**, OAc^- **5**). We also wish to report the synthesis of the first unsymmetrical PCP′ pincer bis(phosphinite) 1-($^iPr_2PO$)-3-($^iPr_2POCH_2$)(C_6H_4) (**7**) and its palladium(II) complexes: [PdX{(C_6H_3)(OP^iPr_2)-2-($CH_2OP^iPr_2$)-6}] (X = Cl^- **8**, I^- **9**, OAc^- **10**). The X-ray structure of **8** has been solved and is compared to that of **1**, which has been published [5d].

* Corresponding author. Tel.: +1-808-534-7064; fax: +1-808-543-8182.
E-mail addresses: chmre@gold.chem.hawaii.edu (M.R. Eberhard), yyama@sci.hiroshima-u.ac.jp (Y. Yamamoto).
[1] To whom correspondence pertaining to crystallographic studies should be addressed.

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These complexes were applied to the allylic alkylation of cinnamyl acetate with sodium dimethyl malonate. Catalytic allylic alkylation is one of the most important reactions in synthetic chemistry. Many advances regarding the regioselectivity and enantioselectivity of this C–C bond forming reaction have been made and several reviews have appeared [10]. Surprisingly, pincer complexes have not been studied for this reaction yet [11]. The activity and selectivity of these new complexes are compared in order to evaluate the influence of the ligand structure and co-ordinating or non-co-ordinating anions on this reaction.

2. Results and discussion

2.1. Ligand synthesis and complexes

[PdCl{(C_6H_3)(OP^iPr_2)$_2$-2,6}] (**1**) was reacted with NaBr or NaI in acetone to give [PdX{(C_6H_3)(OP^iPr_2)$_2$-2,6}] (X = Br^- **2**, I^- **3**), with AgOTf in THF and AgOAc in diethyl ether to give [PdX{(C_6H_3)(OP^iPr_2)$_2$-2,6}] (X = OTf^- **4**, OAc^- **5**).

Commercially available 3-hydroxybenzylalcohol **6** is the starting material for the synthesis of ligand **7** (Scheme 1). Addition of two equivalents ClP^iPr_2 to a solution of **6** in THF in the presence of DMAP furnishes the moisture- and air-sensitive ligand after work-up in 84% yield. The reaction of **7** with [$PdCl_2$(cod)] in refluxing toluene gave the cyclometallated complex **8** as a colourless solid after recrystallisation or column chromatography (75% yield). Magnetically inequivalent phosphorus nuclei are observed for **8** in the $^{31}P\{^1H\}$-NMR spectrum with a coupling constant of $^2J(PP')$ 429 Hz clearly indicating the *trans*-disposition of the phosphorus donors. Metathesis reaction with NaI in acetone and AgOAc in diethyl ether gave **9** ($^2J(PP')$ 422 Hz) and **10** ($^2J(PP')$ 446 Hz), respectively.

Complexes **8**–**10** are unusual for pincer complexes in that they are composed of five- and six-membered metallacycles, respectively. To the best of our knowledge they represent the first examples of pincer complexes with different metallacycle ring-sizes. Single crystals of **8**, suitable for X-ray diffraction, were obtained by slow diffusion of pentane into a saturated solution of the complex in dichloromethane. Fig. 1 shows its molecular structure.

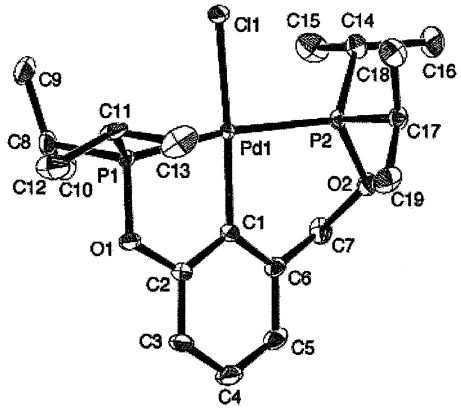
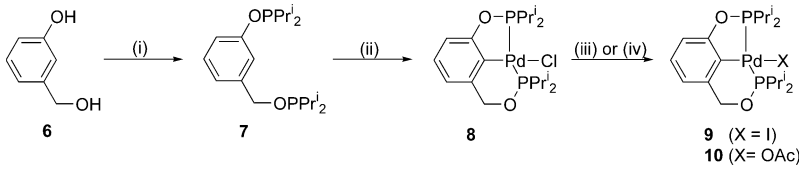


Fig. 1. Displacement ellipsoid plot (50% probability level) of **8**. Hydrogen atoms have been omitted for clarity. Pertinent bond lengths (Å) and angles (°): Pd(1)–Cl(1) 2.370(1); Pd(1)–P(1) 2.2590(9); Pd(1)–P(2) 2.2848(9); Pd(1)–C(1) 2.030(4); Cl(1)–Pd(1)–P(1) 101.17(2); Cl(1)–Pd(1)–P(2) 95.16(2); Cl(1)–Pd(1)–C(1) 176.0(1); P(1)–Pd(1)–P(2) 168.31(5); P(1)–Pd(1)–C(1) 81.3(1); P(2)–Pd(1)–C(1) 91.6(1).

All bond lengths are within the typical range. Note that Pd(1)–P(2) is slightly longer than Pd(1)–P(1) (2.2848(9) Å vs 2.2590(9) Å). The five-membered metallacycle shows the expected distorted envelope conformation whereas the six-membered metallacycle reveals a boat-conformation. A comparison of the structure of **8** with the structure of **1** [5d] reveals the effect of increasing the ring-size of one of the metallacycles. The P–Pd–P bond angles are significantly different: 160.380(6)° for **1** and 168.31(5)° for **8** (P(1)–Pd(1)–P(2)). Whilst the bond lengths are comparable in both structures, it is clear that introducing a larger metallacycle leads to a relaxation of the bond angles.

2.2. Allylic alkylation of cinnamyl acetate with sodium dimethyl malonate

Allylic alkylation with soft nucleophiles has been achieved with many metals e.g. Pd [10], Pt [12], Ir [13], Rh [14], W [15] and Mo [15b,16]. Palladium is by far the most popular choice for catalysts, which are usually stabilized with monodentate or bidentate ligands. Moreover, it has been found that anions can affect regio- and enantioselectivity e.g. Cl^- [17] and I^- [18] affect the regioselectivity whereas F^- affects the enantioselectivity [19]. Tridentate monoanionic pincer complexes have not been applied to this reaction yet [11]. Our objective was to study the regioselectivity of this C–C bond forming



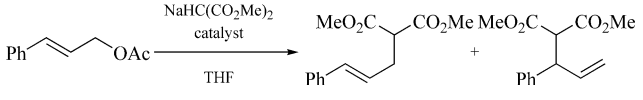
Scheme 1. Synthesis of ligand **7** and complexes **8**–**10**. *Reagents and conditions:* (i) Two equivalents ClP^iPr_2, DMAP, THF, r.t.; (ii) [$PdCl_2$(cod)], THF, reflux; (iii) NaI, acetone, r.t.; (iv) AgOAc, Et_2O, r.t., ultrasound.

reaction with regard to the structure of the ligand and the nature of the anion X i.e. non-co-ordinating or co-ordinating. We chose the standard reaction between cinnamyl acetate with sodium dimethyl malonate for this purpose. Catalytic experiments were conducted in THF at either 25 or 75 °C using 5 mol.% catalyst. A mixture containing cinnamyl acetate and the catalyst in THF was added to sodium dimethyl malonate (generated from sodium hydride and dimethyl malonate in THF) and analysed after the prescribed time. Cationic complexes derived from **8** were generated in situ. The results are summarised in Table 1.

In general the activity of all catalysts are high leading to complete conversions of cinnamyl acetate and isolated yields of about 70%. The formation of the linear isomer clearly dominates (exclusively *trans*). This is not unexpected for palladium catalysts, which mostly lead to reaction at the less hindered terminus of the substrate [20]. Whereas a slightly greater influence of X on the regioselectivity is seen in the case of **1** and its derivatives, no influence is apparent in case of **8** and its derivatives. Cationic catalyst **4** gives the largest amount of isomerisation (entry 5; 83:17). This is in contrast to a system of **8**/AgOTf, which under the same conditions leads to very little isomerisation (entry 12; 95:5). Whilst these results do not constitute an advance in allylic alkylation chemistry, a detailed look into the activity of these complexes revealed interesting trends regarding these pincer catalysts. These results are shown in Fig. 2.

Indeed the activity of these catalysts are very much dependent on the structure of the ligand and the nature of X. Catalyst **1** and derivatives thereof show only reasonable activity at higher temperatures, whereas **8**

Table 1
Regioselectivity in the allylic alkylation of cinnamyl acetate with sodium dimethyl malonate



Entry	Catalyst	T (°C)	t (h) [a]	Linear:branched
1	**1**	25	72	96:4
2	**1**	75	16	95:5
3	**2**	75	16	90:10
4	**3**	75	16	97:3
5	**4**	75	16	83:17
6	**5**	75	16	94:6
7	**8**	25	12	94:6
8	**9**	25	12 [b]	93:7
9	**10**	25	6	94:6
10	**8**/$AgBF_4$	25	6	94:6
11	**8**/AgOTf	25	6	94:6
12	**8**/AgOTf	75	16	95:5

[a] 100% conversion.
[b] 82% conversion.

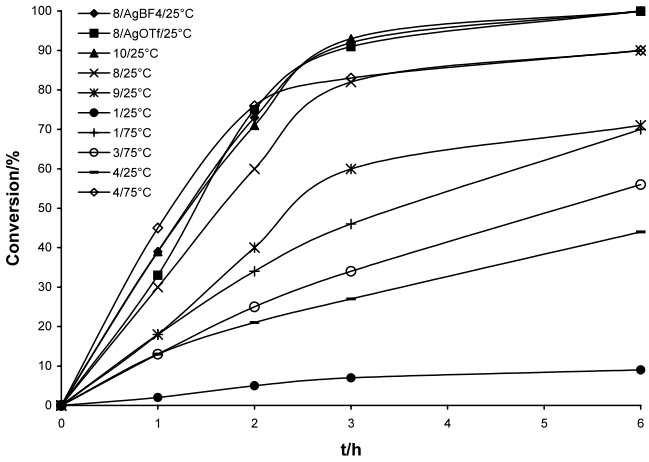


Fig. 2. Plot of conversion vs time for various catalyst systems.

and derivatives are highly active at room temperature. At room temperature, as well as 75 °C, the activity for **1** and its derivatives increases with decreasing co-ordination strength of X i.e. $I^- < Cl^- < OTf^-$. At 75 °C only cationic complex **4** achieves comparable activity to **8**/AgOTf, **8**/$AgBF_4$ and **10**, with ca. 90% conversion after 6 h. Catalytic systems **8**/AgOTf, **8**/$AgBF_4$ and **10** behave identically and are most active giving complete conversion after 6 h. Catalysts **8** and **9** give 90 and 71% conversion, respectively after 6 h; 100% conversion is achieved after 12 h with **8**, whereas catalyst **9** achieves only 82% conversion after 12 h. In comparison the activity of **1** is rather low at 25 °C with only 9% conversion after 6 h. Even at 75 °C catalysts **1** and **3** only give 70 and 56% conversion after 6 h (80 and 71%, respectively after 10 h) showing that the activity of **1** and derivatives thereof is significantly lower than that of **8** and its derivatives. Interestingly the activity of catalysts **1** and **3** is always lower than that of catalysts **8** and **9**, respectively. The activity of catalysts **8** and derivatives increases with the metal centre being more easily accessible e.g. in the order **9** < **8** < **10** ≈ **8**/AgOTf ≈ **8**/$AgBF_4$.

In order to test if the mechanism of this reaction involves an allyl intermediate or a discreet enyl-species ($\sigma+\pi$) the reaction of allylic deuterated acetate **11** with sodium dimethyl malonate was examined (Fig. 3). A similar labeling experiment has been conducted by Evans and Nelson who observed for the first time enyl intermediates in acyclic rhodium-catalysed allylic alkylation [14a].

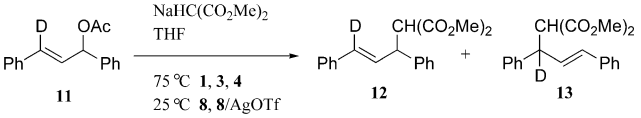


Fig. 3. Deuterium-labeling experiment in order to test if an allyl-mechanism is present.

^{1}H-NMR analysis of the product after column chromatography shows that 1:1 ratios of **12**:**13** are always obtained independent of the catalyst used. This indicates that allyl intermediates are most likely formed in this reaction with cationic and neutral catalyst precursors. As is common in allylic alkylation the allylic acetate is oxidatively added to the Pd(II) centre to form a palladium allyl species and consequently reacts with the nucleophile to yield the product. The presence or absence of other ligands besides the PCP or PCP′ ligand influences the activity of the catalysts directly. Weaker co-ordinating anions lead to more reactive catalyst species. This is obvious as the first step must be co-ordination of the allylic acetate to the metal centre upon which it is then oxidatively added. It is not clear yet if co-ordinating anions such as halides dissociate from the metal centre or remain co-ordinated during the catalytic cycle. Thus, a question which still needs to be answered is if either intimate ion-pairs such as $[PdPCP(allyl)X]^+[OAc^-]$ or $[PdPCP(allyl)]^{2+}[X^-][OAc^-]$ or solvent separated ion-pairs such as $[PdPCP(allyl)X]^+||[OAc^-]$ or $[PdPCP(allyl)]^{2+}||[X^-]||[OAc^-]$ are formed when X is a halide. Ongoing experiments in our laboratories with the platinum analogues of **1** and **8** are addressing this question. Preliminary results show that residues of experiments with **1**, **3**, **8** and **10**, which were examined spectroscopically by $^{31}P\{^1H\}$-NMR after the reaction had finished, only had the original catalysts present. Halides were not displaced by acetate although a large excess of acetate is present in the reaction mixture. Furthermore, an in situ $^{31}P\{^1H\}$-NMR study of the allylic alkylation reaction using **1** and **4** at 75 °C and **8**, **8**/$AgBF_4$, **8**/AgOTf and **10** at room temperature as catalysts only showed species to be present of which one is the starting material complex and the others can be tentatively assigned to alkene co-ordination product and oxidative addition product. Especially for the experiments with **8**, **8**/$AgBF_4$, **8**/AgOTf and **10** only *trans*-co-ordinated species are observed (typical coupling constants of 400–500 Hz). In none of the experiments do we observe phosphorus ligand dissociation or ring-opening [21].

Interestingly, **8** and derivatives thereof prove to be more active than complex **1** and its derivatives. We think this can be attributed to two facts: Complexes of **7** are electronically different to complexes of 1,3-(^{i}Pr$_2$PO)$_2$(C_6H_4) simply due to the fact that one donor is an aryl dialkylphosphinite, the other an alkyl dialkylphosphinite. But more importantly, comparing bond angles of complexes of **1** and **8** shows that the PMP angle for **8** is significantly larger by 8°. Ligand bite angles (or P–M–P angles) for metal complexes with bidentate phosphorus ligands have been studied extensively over the last 25 years. Dierkes and van Leeuwen stated that they are a useful parameter for the explanation of observed rates and selectivities of catalytic reactions [22]. One important observation is that if the ligand bite angle is close to that expected for the transition state of a reaction, the activation energy for this step should be lower and the reaction step is accelerated. If in fact this step is rate determining, the catalytic cycle runs more smoothly and with higher frequency. In the case of the ligand bite angle being close to that of the reactant or product complex the energy of the transition state will be higher and the energy of the starting material is less affected. Owing to increased activation energy the reaction is slower. van Leeuwen and co-workers have studied the effect of the bite angle of diphosphine ligands on activity in palladium-catalysed allylic alkylation [23]. They observed an increase in activity with increasing bite angles. It has to be noted, however, that the ligands studied co-ordinate in a *cis*-fashion to the metal whereas the ligands in this study are monoanionic terdentate ligands with the phosphorus co-ordinated *trans* to each other. Nevertheless, we also observe an increase in activity with an increase in the P–M–P angle. The larger P–M–P angle and the more flexible structure of **8** and its analogues is more suited for oxidative addition of allyl acetates leading to better conversions and a more efficient reaction than that of **1** and its analogues.

In fact, one may expect that palladium pincer complexes of 1,3-(^{i}Pr$_2$POCH$_2$)$_2$(C_6H_4) with two six-membered metallacycles will show even higher activity in allylic alkylation than any of the complexes in this study. Ligand 1,3-(^{i}Pr$_2$POCH$_2$)$_2$(C_6H_4) is prepared in a straightforward manner from 1,3-(HOCH$_2$)$_2$(C_6H_4). However, the reaction of this ligand with either [$PdCl_2$(cod)] or [$PdCl_2$(NCPh)$_2$] did not give the desired pincer complex but only polymeric species. We are in the process of developing a different approach towards [PdX{(C_6H_3)(CH$_2$OP^{i}Pr$_2$)$_2$-2,6}] in order to complete this study.

3. Conclusion

In conclusion we have prepared the novel unsymmetrical pincer ligand **7**. A series of palladium(II) complexes derived from this ligand were compared to complexes derived from the symmetrical pincer analogue 1,3-(^{i}Pr$_2$PO)$_2$(C_6H_4). All complexes were applied and found to be active catalysts for the allylic alkylation of cinnamyl acetate with sodium dimethyl malonate. They show little isomerisation activity giving only linear product. However, palladium complexes of **7** are significantly more active catalysts than palladium complexes of 1,3-(^{i}Pr$_2$PO)$_2$(C_6H_4). We attribute this increase in activity to the introduction of a six-membered metallacycle into the pincer complex structure. This in

turn leads to a more flexible complex structure and an increase in the P–M–P angle. Moreover, the catalytic activity depends strongly on the presence or absence of co-ordinating anions.

4. Experimental

4.1. General procedure

All manipulations were carried out using standard Schlenk procedures under nitrogen. Solvents (CH_2Cl_2, toluene, THF, diethyl ether) were freshly distilled from either CaH_2 or K/benzophenone under nitrogen. 3-Hydroxybenzylalcohol, 4-dimethylaminopyridine DMAP, chlorodiisopropylphosphine, pyridine, acetic anhydride, dimethyl malonate, cinnamyl alcohol, silver triflate, silver tetrafluoroborate and sodium hydride were purchased from Aldrich and used without further purification. Silver acetate was purchased from Mallinckrodt. Silica gel (100–200 mesh), alumina, celite 545 and magnesium sulfate were purchased from Fisher Scientific. [$PdCl_2$(cod)] was prepared according to a previously published method [24]. Complex **1** was prepared according to the published procedure [5d].

^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectra were recorded on a Varian Unity Inova 300 spectrometer at ambient temperature of the probe using the deuterated solvent to provide the field/frequency lock. Chemical shifts are reported in parts per million relative to high frequency of TMS for ^{1}H and ^{13}C{^{1}H} and relative to high frequency of 85% H_3PO_4 for ^{31}P{^{1}H} — elemental analysis were performed by Oneida Research Services.

Identity and purity of the products in the catalysis experiments were determined by gas chromatography with a gas chromatograph GC HP 5980A with flame ionization detector (FID), equipped with a HP-1 capillary column (25 m) from Hewlett Packard, by gas chromatography with a gas chromatograph GC HP 5890 Series II with a mass selective detector HP 5971 (GC–MS), equipped with a HP-1MS capillary column (30 m) from Hewlett Packard, and by NMR spectroscopy on a Varian Unity Inova 300 spectrometer.

4.1.1. Ligand and complex synthesis

*4.1.1.1. 1-(^{i}Pr$_2$PO)-3-(^{i}Pr$_2$POCH$_2$)(C_6H_4) (**7**).* To a solution of 3-hydroxybenzylalcohol **6** (0.124 g, 1 mmol) and DMAP (0.244 g, 2 mmol) in THF (20 ml) was added dropwise with stirring Cl$P^i Pr_2$ (0.305 g, 0.318 ml, 2 mmol) at room temperature (r.t.). A precipitate formed immediately and the mixture was stirred overnight. The solvent was removed in vacuum and the residue extracted repeatedly with toluene. The toluene extracts were filtered over celite and the filtrate was concentrated in vacuum to give **7** (0.299 g, 0.84 mmol, 84%) as a colourless oil. ^{1}H-NMR (300 MHz, CD_2Cl_2): $\delta = 0.89$–1.10 (m, 12H, CH(CH_3)$_2$), 1.58–1.70 (m, 1H, CH(CH$_3$)$_2$), 1.71–1.98 (m, 1H, CH(CH$_3$)$_2$), 4.61 (ABX, 2H, CH_2O), 6.82–7.14 (m, 4H, ArH) — ^{13}C{^{1}H}-NMR (75 MHz, CD_2Cl_2): $\delta = 16.96$, 17.04, 17.6, 17.8, 17.9, 18.1, 28.2, 28.4, 28.6, 74.2 (d, $J = 34$ Hz, CH_2O), 114.7, 118.0, 117.8, 117.7, 120.7, 129.3, 141.5 (d, $J = 8$ Hz), 159.7 (d, $J = 8$ Hz) — ^{31}P{^{1}H}-NMR (121 MHz, CD_2Cl_2): $\delta = 150.8$ ($C_{Ar}OP^iPr_2$), 156.0 ($CH_2OP^iPr_2$).

*4.1.1.2. [PdCl{(C_6H_3)(OP^iPr_2)-2-($CH_2OP^iPr_2$)-6}] (**8**).* To a suspension of [$PdCl_2$(cod)] (0.285 g, 1 mmol) in toluene (10 ml) was added dropwise with stirring a solution of **7** (0.356 g, 1 mmol) in toluene (10 ml). The suspension was refluxed for 4 h during which time a clear yellow solution formed. The solvent was removed in vacuum and the solid was dissolved in CH_2Cl_2 and filtered over a short SiO_2 pad to give **8** (0.373 g, 0.75 mmol, 75%) as a pale yellow solid, which can be recrystallised from diethyl ether. Single crystals were grown from CH_2Cl_2/pentane. ^{1}H-NMR (300 MHz, CD_2Cl_2): $\delta = 1.14$ (dd, 6H, $^1J = 13.8$ Hz, $^2J = 6.9$ Hz, CH(CH_3)$_2$), 1.29 (dd, 6H, $^1J = 14.4$ Hz, $^2J = 6.9$ Hz, CH(CH_3)$_2$), 1.36 (dd, 6H, $^1J = 7.2$ Hz, $^2J = 2.4$ Hz, CH(CH_3)$_2$), 1.42 (dd, 6H, $^1J = 7.2$ Hz, $^2J = 3.0$ Hz, CH(CH_3)$_2$), 2.37–2.60 (m, 2H, CH(CH$_3$)$_2$), 4.78 (d, $J =$ 18.0 Hz, 2H, CH_2O), 6.69–7.4 (m, 3H, ArH) — ^{13}C{^{1}H}-NMR (75 MHz, CD_2Cl_2): $\delta = 16.7$, 16.9, 17.3, 17.4, 18.3, 18.4, 27.6, 27.7, 27.9, 28.0, 28.6, 28.7, 28.86, 28.94, 78.1 (d, $J = 3$ Hz, CH_2O), 112.2 (d, $J = 14$ Hz), 121.3, 126.5, 132.9, 139.1 (d, $J = 11$ Hz), 168.1 (d, $J = 14.9$ Hz) — ^{31}P{^{1}H}-NMR (121 MHz, CD_2Cl_2): $\delta = 189.6$ (d, $^2J = 429$ Hz, $C_{Ar}OP^iPr_2$), 151.4 (d, $^2J = 429$ Hz, $CH_2OP^iPr_2$) — C: 46.06 (45.89) H: 6.69 (6.69).

*4.1.1.3. [PdX{(C_6H_3)(OP^iPr_2)$_2$-2,6}] (X = Br^- **2**, I^- **3**) [PdI{(C_6H_3)(OP^iPr_2)-2-($CH_2OP^iPr_2$)-6}] (**9**).* A solution of either complex **1** or **8** in acetone was treated with excess NaX and stirred for several hours. Filtration and evaporation of the solvent yielded the respective complexes. ^{1}H-NMR spectra of the products are identical to the starting material ^{1}H-NMR spectra — ^{31}P{^{1}H}-NMR (121 MHz, CD_2Cl_2): $\delta = 190.3$ (**2**); 194.2 (**3**); 195.1 (d, $^2J = 422$ Hz, $C_{Ar}OP^iPr_2$), 154.1 (d, $^2J = 422$ Hz, $CH_2OP^iPr_2$) (**9**).

*4.1.1.4. [PdOTf{(C_6H_3)(OP^iPr_2)$_2$-2,6}] (**4**).* A solution of complex **1** in THF was treated with one equivalent of AgOTf and stirred for 1 h. Filtration through celite and evaporation of the solvent yielded the product. ^{1}H-NMR spectrum are of the product is identical to the starting material ^{1}H-NMR spectrum — ^{31}P{^{1}H}-NMR (121 MHz, CD_2Cl_2): $\delta =$ 189.9.

*4.1.1.5. [PdOAc{(C_6H_3)(OP^iPr_2)-2,6}] (**5**); [PdOAc{(C_6H_3)(OP^iPr_2)-2-($CH_2OP^iPr_2$)-6}] (**10**).* A solution of either complex **1** or **8** in diethyl ether was sonicated in the presence of AgOAc for 30 min. Filtration and evaporation of the solvent yielded the respective complexes. ^{1}H-NMR spectra of the products are identical to the starting material ^{1}H-NMR spectra. NMR data (**5**) — ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.18–1.27 (m, 24H, $CH(CH_3)_2$), 1.90 (s, 3H, CH_3COO^-), 2.41 (m, 4H, $CH(CH_3)_2$), 6.42 (d, J = 8 Hz, 2H, Ar*H*), 6.87 (t, J = 8 Hz, 1H, Ar*H*) — ^{31}P{^{1}H}-NMR (121 MHz, $CDCl_3$): δ = 187.5 — (**10**) — ^{31}P{^{1}H}-NMR (121 MHz, THF, C_6D_6): δ = 184.4 (d, ^2J = 446 Hz, $C_{Ar}OP^iPr_2$), 151.5 (d, ^2J = 446 Hz, $CH_2OP^iPr_2$).

4.2. Allylic alkylation experiments

To a suspension of NaH (10 mg, 0.44 mmol) in THF (1 ml) was added dimethyl malonate (46 μl, 0.4 mmol). The mixture was stirred for 5 min and then transferred to a Schlenk tube with a stir bar. To this was added the Pd catalyst (0.01 mmol) (and one equivalent of a silver salt) and cinnamyl acetate (34 μl, 0.2 mmol) or *trans*-1,3-diphenyl-3-deuterium-2-propenyl-1-acetate **11** (50.3 mg, 0.2 mmol) in THF (1 ml). Undecane (10 μl, 0.047 mmol) was used as internal standard. The tube was then sealed and the mixture was stirred for the prescribed time at r.t. or immersed in a silicon oil bath at 75 °C, respectively. The reaction mixture was analysed by GC–MS. The products were isolated via column chromatography.

*4.2.1. PhCD=CHCH(OAc)Ph (**11**)*

PhC≡CCH(OH)Ph was prepared from phenylacetylene (deprotonated with BuLi) and benzaldehyde in THF and obtained as a colourless oil after column chromatography. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 5.37–5.40 (m, 1H), 6.38–6.42 (m, 1H), 7.23–7.47 (m, 10H, Ar*H*) — ^{13}C{^{1}H}-NMR (75 MHz, CD_2Cl_2): δ = 143.3, 136.8, 131.9, 128.8, 128.0, 127.9, 126.7, 126.5, 89.3, 86.4, 75.1, 75.0.

PhCD=CHCH(OH)Ph was prepared according to a similar procedure by Grant and Djerassi [25]. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.39 (d, 1H, ^3J = 6.6 Hz), 6.40 (m, 1H), 7.23–7.47 (m, 10H, Ar*H*) — ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 141.2, 131.9, 128.9, 128.63, 128.55, 127.5, 126.9, 126.2, 122.7, 68.0, 65.0.

PhCD=CHCH(OH)Ph was dissolved in diethyl ether. Acetic anhydride, triethylamine and a catalytic amount of DMAP were added and the reaction mixture was stirred for 3 h. Typical work-up gave **11** as a colourless solid after column chromatography. ^{1}H-NMR of **11** and comparison to the ^{1}H-NMR of PhCH=CHCH(OAc)Ph shows the absence of desired proton. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.14 (s, 3H), 6.33 (m, 1H), 6.44 (m, 1H), 7.25–7.4 (m, 10H, Ar*H*) — ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 139.7, 128.8, 128.3, 127.8, 127.7, 126.8, 110.0, 76.3, 21.3 (+ overlapping signals in the aromatic region).

4.3. X-ray data collection and structure determination

Crystals of **8** suitable for X-ray analysis were obtained from slow diffusion of pentane into a saturated solution of **8** in CH_2Cl_2. Intensity data were collected at 200 K on a Mac Science DIP2030 imaging plate equipped with graphite-monochromated Mo–K_α radiation (λ = 0.71073 Å). Unit cell parameters were determined by autoindexing several images in each data set separately with program DENZO. For each data set, rotation images were collected in 3° increments with a total rotation of 180° about ϕ. Data were processed by using SCALEPACK. The structure was solved using the teXsan system and refined by full-matrix least-squares (Table 2).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 205746 for compound **8**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-

Table 2
Crystallographic data

Compound	**8**
Empirical formula	$C_{19}H_{33}ClO_2P_2Pd$
M	497.27
Temperature (K)	200
Colour	yellow
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	8.2150(1)
b (Å)	11.0300(2)
c (Å)	13.0140(3)
α (°)	102.455(1)
β (°)	95.322(1)
γ (°)	90.691(1)
U (Å^3)	1145.88(4)
Z	2
μ Mo–K_α (cm^{-1})	1.076
Crystal dimensions (mm)	0.350 × 0.200 × 0.150
θ Range (°)	12.6–27.9
No. of data/restraints/parameters	3841/0/226
No. of reflections observed	3950
Final R_2 and wR_2 indices [a]	0.0344, 0.0992
Conventional R index [$F^2 > 3\sigma(F^2)$] [a]	0.0344
Reflections with $F^2 > 3\sigma(F^2)$	3841
Goodness-of-fit	1.069

[a] $w = 1/[\sigma^2(F_o) + 0.0856(F_o)^2]$.

mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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